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Electronic states of *A*-site ordered double perovskite $YBaCo_2O_x$ (x = 5.3 and 6) thin films investigated by X-ray spectroscopy

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1 Introduction

A-site double perovskite cobaltite $RBaCo_2O_x$ (*R* = rare earth element), in which the *A*-site cations *R* and Ba order along the *c*-axis, exhibits intriguing electronic and electrochemical properties, such as spin crossover, high magnetoresistance, and high electronic and ionic conductivities, and these properties are strongly affected by the ionic size of *R* and the oxygen content (x). In particular, as the ionic size of *R* decreases, the Co 3*d* orbitals distort more with the shrinking of the *c*-axis, leading to a rich variety of electronic phases. Indeed, *A*-site-ordered $YBaCo_2O_x$ with a small Y ion shows Co^{2+}/Co^{3+} charge ordering (x = 5.0) [1], spin-state ordering between low and high spin-state Co^{3+} ions (x =5.5) [2], and metallicity and in-plane ferromagnetism with a Curie temperature of 130–140 K [3,4]. Furthermore, $YBaCo_2O_6$ thin films exhibit huge magnetic anisotropy with a magnetic anisotropy constant of 1.5 × 10^8 erg cm^{-3}, which is comparable to that of $SmCo_5$ [3].

In this study, we investigated the electronic states of ferromagnetic metallic $YBaCo_2O_6$ and antiferromagnetic insulating $YBaCo_2O_{5.3}$ epitaxial thin films by X-ray absorption spectroscopy (XAS), X-ray photoemission spectroscopy (PES), and X-ray magnetic circular dichroism (XMCD) measurements.

2 Experiment

$YBaCo_2O_{5.3}$ epitaxial thin films were grown on $SrTiO_3$(001) substrates by pulsed laser deposition (PLD). The obtained films were subjected to successive topotactic oxidation using a NaClO aqueous solution to prepare $YBaCo_2O_6$ thin films. The typical film thicknesses were measured to be 60–80 nm using a stylus surface profiler.

The PES and XAS measurements were performed at a pressure of ~1 × 10^{-10} Torr and 200 K for the $YBaCo_2O_6$ film and 300 K for the $YBaCo_2O_{5.3}$ film at the undulator beamline BL-2A. The PES spectra were collected using a VG-SCIENTA SES-2002 electron-energy analyzer. The Fermi energy of an *in situ* evaporated gold film was used for energy interference. The XMCD measurements of the $YBaCo_2O_6$ thin film were performed at a pressure of ~1 × 10^{-9} Torr and temperatures 30 K and 200 K using a vector-magnet XMCD apparatus with circularly polarized soft X-rays at the helical undulator beamline BL-16A2. The strength of the applied magnetic field was 5 T. The XAS and XMCD spectra were measured in the total electron yield mode.

3 Results and Discussion

The valence numbers and spin states of Co in $YBaCo_2O_x$ (x = 5.3 and 6) thin films were determined by Co $L_{2,3}$ XAS measurements. Figure 1 shows the Co $L_{2,3}$ and Ba $M_{4,5}$ XAS spectra of the $YBaCo_2O_6$ and $YBaCo_2O_{5.3}$ films measured at 200 K and 300 K, respectively. The figure also includes the spectra of $BaFeO_3$, Sr_2CoO_3Cl, $SrCoO_3$, and CoO as references for Ba^{2+}, high-spin (HS) Co^{3+}, intermediate spin (IS) Co^{4+}, and HS Co^{2+}, respectively [5–7]. The observed XAS spectra were well reproduced by a linear combination of referenced XAS spectra normalized by the areas. The Co *L*-edge XAS spectrum of the $YBaCo_2O_6$ thin film was well fitted with a superposition of 50% HS Co^{3+} and 50 % IS Co^{4+}, indicating that the Co valence number in the $YBaCo_2O_6$ film is ~3.5 [3]. Moreover, the best fit to the spectrum of the $YBaCo_2O_{5.3}$ thin film was obtained by assuming a superposition of 80% HS Co^{3+} and 20% HS Co^{2+}, yielding an average Co valence of ~2.8. These Co valences are in good agreement with those calculated from the nominal compositions, 3.5 and 2.8, respectively.

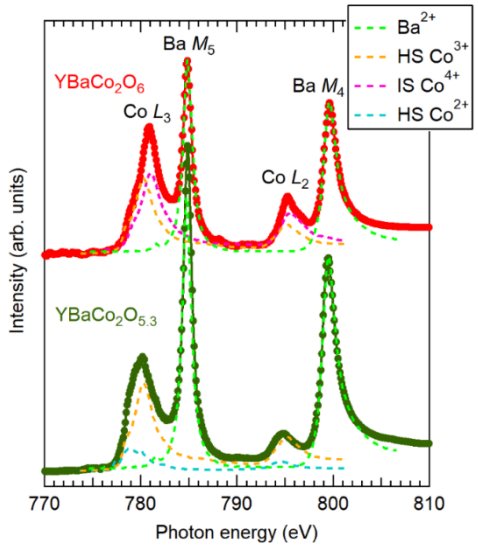

Fig. 1: Co $L_{2,3}$ and Ba $M_{4,5}$ XAS spectra of the thin films of $YBaCo_2O_6$ and $YbaCo_2O_{5.3}$ at 200 K (red solid line) and 300 K (green solid line), respectively. The light green, orange, pink, and light blue dashed lines are references for Ba^{2+} ($BaFeO_3$ [5]), HS Co^{3+} (Sr_2CoO_3Cl [6]), IS Co^{4+} ($SrCoO_3$ [7]), and HS Co^{2+} (CoO [6]), respectively. Reproduced from [8], with the permission of AIP Publishing.

Figure 2(a) shows polarization-dependent XAS spectra of the $YBaCo_2O_6$ thin film around the Co $L_{2,3}$ edges obtained at 30 K, where μ_+ and μ_- denote the absorption coefficients for photon helicity parallel and antiparallel to the Co 3*d* majority-spin direction, respectively. The spectra were normalized by the peak height of Ba M_5 structure, which does not show XMCD. The inset of Fig. 2(a) shows a sketch of the XMCD experiment geometry. In this geometry, the obtained XMCD signal reflects the in-plane [110] magnetization. As shown in Fig. 2(a), an XMCD signal was detected at the Co $L_{2,3}$ edges, indicating that $YBaCo_2O_6$ is ferromagnetic at 30 K. In contrast, no XMCD signal was detected at 200 K, which is consistent with the result of magnetization measurement revealing ferromagnetic-paramagnetic transition at 130 K [3].

Figure 2(b) shows an XMCD spectrum ($\Delta\mu = \mu_+ - \mu_-$) of the $YBaCo_2O_6$ thin film at 30 K. Notably, the Co L_3 XMCD signal observed in the photon energy area of 776.2 to 782.5 eV split into two peaks separated by 1 eV, with almost the same intensity. Referring to the XAS spectrum shown in Fig. 1, these two peaks can be assigned to the XMCD components from Co^{3+} and Co^{4+}. Thus, it is concluded that both spin states contribute to the ferromagnetism of $YBaCo_2O_6$. From the spectrum, the orbital and spin magnetic moments (M_{orb} and M_{spin}) were estimated to be 0.046 μ_B/Co and 0.17 μ_B/Co using XMCD sum rules [9]. The total magnetic moment ($M_{total} = M_{orb} + M_{spin}$) was 0.22 μ_B/Co, which is smaller than the saturated moment of 0.75 μ_B/Co, determined by *M*–*H* measurements at 5 K under *H* along the [110] direction [3]. This discrepancy can be attributed to the presence of a nonmagnetic surface layer because the probing depths of XAS and XMCD are much smaller than the film thickness [10]. Here, we focus on the M_{orb} / M_{spin} ratio, which is less influenced by the non-magnetic surface dead layer. The M_{orb} / M_{spin} ratio of the $YBaCo_2O_6$ thin film was estimated to be 0.27. According to the ionic model reported by Okamoto *et al*. [11], wherein three different spin states (low-spin (LS), HS, and IS) were considered for Co^{3+} and Co^{4+} ions, the M_{orb} / M_{spin} ratios of LS Co^{3+}, LS Co^{4+}, IS Co^{3+}, IS Co^{4+}, HS Co^{3+}, and HS Co^{4+} can be calculated as 0, 2.236, ≲0.5, ≲0.33, 0.215, and ~10^{-3}, respectively [11]. The experimentally observed M_{orb} / M_{spin} ratio for the $YBaCo_2O_6$ thin film (0.27) does not contradict the expected value of HS Co^{3+} or IS Co^{4+}, supporting the claim that ferromagnetism arises from the HS Co^{3+} and IS Co^{4+} mixed states.

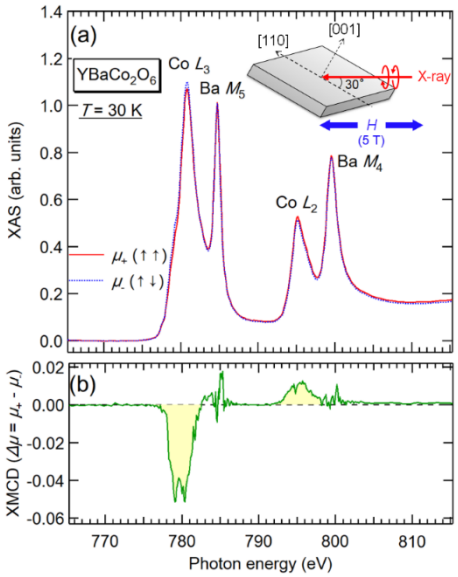

Fig. 2: (a) Polarization-dependent XAS spectra of the $YBaCo_2O_6$ thin film around the Co $L_{2,3}$ edges at 30 K. The XMCD experiment geometry is also shown. These spectra were normalized by the peak height of the Ba M_5 peaks. (b) Co $L_{2,3}$-edges XMCD spectrum of the $YBaCo_2O_6$ thin film. Reproduced from [8], with the permission of AIP Publishing.

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